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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09K 3/14, C04B 35/565, B24D 3/14	**A1**	(11) International Publication Number: **WO 95/03370** (43) International Publication Date: 2 February 1995 (02.02.95)

(21) International Application Number: PCT/US94/07801

(22) International Filing Date: 14 July 1994 (14.07.94)

(30) Priority Data:
08/096,341   22 July 1993 (22.07.93)   US

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(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN,
CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU,
LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD,
SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE,
DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI
patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE,
SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the
claims and to be republished in the event of the receipt of
amendments.

(54) Title: SILICON CARBIDE GRAIN

(57) Abstract

A sintered, polycrystalline silicon carbide abrasive grain having essentially no free silicon.

SILICON CARBIDE GRAIN

BACKGROUND OF THE INVENTION

Silicon carbide abrasive grain typically is produced by the well known Acheson process. In this process, silica sand and petroleum coke are packed around a

5 conductive graphite core which is resistively heated with an electric current. During heating to the high temperatures achieved within the packed bed, the reaction of carbon and silica results in the formation of a silicon carbide ingot. This ingot is separated from the

10 graphite core and unreacted sand and subsequently crushed into useful shapes and sizes to produce conventional silicon carbide grain. The quality of the silicon carbide grain made from this process is determined by the purity of the feed material, the method of packing the

15 furnace feed bed, the temperature history followed in the firing cycle, and the crushing and post treatments used in producing grains.

In the Acheson process, graphite, silicon metal, silica, metallic carbides and other oxide mineral phases

20 are typically formed as reaction byproducts in the furnace bed. These contaminant phases are codeposited and entrained within the silicon carbide which is the primary reaction product produced in the furnace. Thus, the quality of silicon carbide grain produced by this

25 process is also generally dependent on the presence and elimination of extraneous phases and contaminants during the subsequent processing operations of crushing, sizing, floatation, chemical treatment and washing.

As mentioned above, one factor which influences the

30 quality of conventional silicon carbide grains is the mechanical crushing operations which are required to reduce the size of the massive silicon carbide crystals which form in the Acheson furnace to useful grit sizes used in abrasive products. The severe mechanical forces

required for crushing large silicon carbide crystals into useful grit sizes introduce dislocations and microcracks as defects in conventional silicon carbide grain. These defects, as well as any inclusions of the residual

5   contaminant material phases from the furnacing operation, act as characteristic flaws which tend to degrade the hardness, toughness and strength of conventional grains which are generally monocrystalline.

When used in grinding wheels, the conventional

10   silicon carbide abrasive grains produced by the above process exhibit certain deficiencies. Because these monocrystalline grains are intrinsically brittle in nature, they fracture under normal grinding loads, leading to catastrophic cleavage of the grain and

15   accelerated removal of grain material from the grinding wheel during use. Inclusions of other phases and the mechanical crushing operations used in producing conventional grains introduce crystal defects and flaws in these grains which tend to weaken the material further

20   and compromise its performance in grinding applications. Inclusions of contaminant phases may also increase the reactivity of the grain to the workpiece during grinding of certain materials and further degrade grinding performance due to chemical reactions between the grain

25   and workpiece. In addition, conventional silicon carbide grains produced by the Acheson process typically have a smooth surface texture due to the fracture and cleavage of monocrystals during the crushing operation. This smooth surface texture prevents effective bonding of the

30   grain and matrix phase in most abrasive products and promotes grain pullout and accelerated wheel wear during grinding operations.

The prior art has attempted to improve upon the conventional monocrystalline silicon carbide grains

35   produced by the Acheson process by other processing routes. For example, U.S. Patent No. 3,480,395 (McMullen et al.) extrudes a green body of fine silicon carbide

powder, excess carbon and a temporary binder, and fires
it in the presence of free silicon to produce a
polycrystalline, siliconized silicon carbide grain.
However, the grain produced by this process suffers from
5   many deficiencies. In particular, the presence of free
silicon in the final grain increases the reactivity of
the grain toward most alloy materials, makes the grain
susceptible to undesirable oxidation in a typical
grinding application environment, decreases the hardness
10 of the grain and severely degrades the grain's grinding
performance at the high temperatures encountered at the
abrasive-workpiece interface.

Thus, it is an object of the present invention to
produce a silicon carbide grain having improved
15 mechanical and chemical properties for abrasive
applications.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is
provided a sintered, polycrystalline silicon carbide
20 abrasive grain having essentially no free silicon. In
some embodiments of the present invention, the silicon
carbide abrasive grain has a textured surface.

Also in accordance with the present invention, there
is provided a process for producing silicon carbide
25 grains comprising the steps of:

a) forming a shape from a formulation comprising
silicon carbide powder,

b) crushing the shape to produce silicon carbide
grains, and

30 c) sintering the grains either before or after
crushing the shape.

In further accordance with the present invention,
there is provided either a composite or an abrasive
article, including but not limited to, a coated abrasive,
35 a grinding wheel, a lapping compound, an abrasive pad,
and an abrasive fabric, comprising the silicon carbide
abrasive grains.

DESCRIPTION OF THE FIGURES

Figures 1-3 are photographs of textured surfaces of abrasive grains of the present invention.

Figure 4 presents properties of the abrasive grains

5   of the present invention and comparitive example grains.

Figure 5 presents vitrified grinding wheel properties for the abrasive grains of the present invention and comparitive example grains.

Figure 6 presents grinding wheel performance data

10   for the abrasive grains of the present invention and comparitive example grains.

DETAILED DESCRIPTION OF THE INVENTION

The formulation comprising silicon carbide powder and at least one sintering aid usually includes

15   conventional additives. Typically, the formulation comprises sintering aids and temporary binders, and may also include dispersants, surfactants, humectants, plasticizers, fungicides and mold release agents. In a preferred embodiment of the present invention, the

20   formulation consists essentially of silicon carbide powder, at least one sintering aid, a binder and water.

The silicon carbide powder of the present invention may be in the alpha form, the beta form, or a mixture thereof. In addition, the form of silicon carbide powder

25   may be either of a green, high purity type or a black, low purity type or mixtures thereof. In preferred embodiments, the alpha form of silicon carbide powder is used. The particle sizing of the powder must be small enough to insure the sinterability of the formulation.

30   Hence, the mean diameter of the silicon carbide powder is typically between about 0.01 and about 3 microns, preferably between about 0.5 and about 1.0 microns, and most preferably about 0.7 microns. Typically, the surface area of the powder is between about 5 and about

35   50 M^2/g, preferably about 10 to 15 M^2/g. In practicing the present invention, α-silicon carbide powders such as

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Norton FCP-10 or FCP-15, manufactured by Norton A/S in
Lillesand, Norway; Stark A10 or A20, manufactured by
Hermann C. Starck, Inc. of New York, NY; and Lonza UF10
or UF20, manufactured by Lonza of Fair Lawn, NJ, may
5   typically be used. β-SiC powders or mixtures of α-SiC
and β-SiC powders may also be used as a starting
material. In preferred embodiments, Norton FCP-15 α-SiC
powder is used. The amount of silicon carbide powder
used in the formulation of the present invention
10   generally constitutes between about 60% and about 99% by
weight of the formulation, preferably between about 90%
and about 98%, and more preferably about 97%.

If it is deemed desirable to reduce the size of
coarse silicon carbide starting materials to promote
15   sinterability, these materials can be milled to a mean
particle size of less than about one micron. This
milling can be performed in water not only in the absence
of organic solvents which protect the silicon carbide
from oxidation, but also without subsequent chemical
20   treatments to remove oxidized silicon carbide or other
contaminants. In preferred embodiments, there is
provided a process for producing a sintered silicon
carbide ceramic comprising the sequential steps of:

a) milling an aqueous slurry of coarse silicon
25   carbide powder at a predetermined pH value of
between about 6.0 and about 10.0 to reduce the mean
particle size of the silicon carbide powder to less
than one micron,

b) adding at least one sintering additive to the
30   aqueous silicon carbide powder slurry,

c) homogeneously mixing the sintering additive with
the aqueous silicon carbide slurry,

d) drying the milled slurry to a moisture content of
less than about 30% by weight of the silicon carbide
35   powder, e) forming a green body from the dried
slurry, and

f) sintering the green body without subjecting the

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green body to chemical treatments which remove oxygen or other impurities.

In preferred embodiments, the milled slurry is dried to produce a concentrate with a moisture content of less than 2% by weight of the silicon carbide powder.

In many embodiments of the present invention, a plurality of sintering aids are used. Preferred sintering aids include boron-based aids and carbon-based aids. However, use of oxide-based aids such as CaO, MgO, BaO, alkaline earth, transition metal or rare earth oxides as sintering aids is also contemplated to be within the scope of the present invention. These sintering aids may be used alone, in combination with one another or together with alumina, silica, phosphate or borate additions. The use of metals, metal carbides, borides, aluminides, silicides, phosphides or combinations of metals, carbides, oxides, aluminates, silicates, phosphates, borates, aluminides, silicides, phosphides and borides as sintering aids is also contemplated to be within the scope of the present invention.

In preferred embodiments of the present invention, the formulation comprises a carbon-based aid and a boron-based aid. The carbon-based aid of this preferred formulation is typically either an organic resin, more preferably Al-5614 resin, manufactured by Borden Industrial Resins of Louisville, KY, or carbon black, more preferably Regal 400 carbon black, manufactured by Cabot Corporation of Billerica, MA. The carbon-based aid typically comprises between about 0.5% and 20% by weight of the formulation of the present invention, preferably between about 1% and about 10%, more preferably between about 2% and about 6%.

The boron-based aid is typically boron carbide or elemental boron, preferably Starck HS Boron Carbide, manufactured by Hermann C. Starck, Inc. of New York, NY. This aid typically comprises between about 0.1% and 30%

by weight of the formulation of the present invention,
preferably between about 0.5% and about 10%, more
preferably between about 0.5% and about 5%.

5   In some formulations of the present invention, the
amounts of the boron-based aid and the carbon-based aid
are substantially greater than conventional usage. In
these embodiments, the boron-based aid is present in an
amount of between about 4 w/o and about 30 w/o of the
formulation, preferably between about 4 w/o and about 10
10   w/o, more preferably between about 4 w/o and about 6 w/o,
while the carbon-based aid is present in an amount of
between about 6 w/o and about 10 w/o of the formulation,
preferably between about 6 w/o and about 8 w/o, more
preferably between about 6 w/o and about 7 w/o.

15   Temporary binders used in accordance with the
present invention typically include polyvinyl alcohol
(PVA), paraffin wax, polyethylene glycol (PEG), starch or
cellulose derivatives, and preferably are either Goshenol
KH-17S PVA (manufactured by Nippon Gohsei, Osaka, Japan),
20   Elvanol 75-15 PVA (manufactured by DuPont Polymers,
Wilmington, DE) or Carbowax 400 PEG (manufactured by
Union Carbide Corp., Danbury, CT). This additive
typically comprises between about 0.1% by weight ("w/o")
and about 10 w/o of the formulation of the present
25   invention, preferably between about 0.25 w/o and 5 w/o.

The formulation comprising silicon carbide powder
and at least one sintering aid can be prepared by any
conventional method. For example, the formulation's
components can be simply mixed in a solvent such as water
30   to form a homogeneous formulation with a predetermined
solids loading which is ready for forming. Typically,
however, the silicon carbide powder is mixed overnight in
a jar roll mill with a pH-adjusted mixture of the
sintering aid, binder and water, wherein the pH is
35   adjusted to between 8.0 and 9.0 by addition of ammonium
hydroxide. Following initial mixing, the formulation can
be subjected to a filtration, spray drying, freeze drying

or oven drying step which removes water from the
formulation. Typically, the formulation is spray dried
in a Niro HT spray drier (Niro Inc., Columbia, MD) which
produces discrete, homogeneous spherical powder

5   agglomerates which create a flowable powder media
amenable to further processing and forming of green
bodies.

        If a green body is formed from the formulation prior
to sintering, that green body can be made by any

10 conventional forming method. For example, the
formulation can be slip cast, injection molded,
dispersion cast, tape cast, sprayed, atomized, nebulized,
or agglomerated in a mixer, extruded, cold uniaxially
pressed or cold isostatically pressed to form the green

15 body.

        In one embodiment of the present invention, the
powder formulation is spray dried and the resulting
spherical agglomerates are sintered to produce dense
spherical grains of fine diameter, ranging in size from 2

20 um to 250 um diameter, where grain size distribution is
controlled by adjusting the spraying conditions in the
spray drier.

        In another embodiment of the present invention, the
spray dried powder formulation is subsequently pelletized

25 in an RO7 Eirich mixer (Eirich Machines Inc., Maple,
Ontario, Canada). The Eirich mixer offers process
control advantages in that it can mix both dry and wet
powders and produce a narrow pellet size distri-bution by
simple adjustment of mixer operating conditions. The

30 powder formulation, which is fed into the mixer with
additions of water and binder, agglomerates into small
seed-like fractions which further agglomerate to larger
sized aggregates to produce dense green pellets ranging
in diameter from about 0.1 mm to about 10.0 mm and

35 typically having densities in the range of 1.5 to 2.0
g/cm^3.

        In another typical method of green body f rmation,

the spray dried powder formulation is mixed with water,
binder, plasticizer, humectant and a mold release agent
to a plastic-like consistency in an Abbe MF sigma-blade
mixer (Paul O. Abbe Inc., Little Falls, NJ) and fed into
5   an extruder to produce extruded green bodies. The
geometric shape of the die orifice of the extruder can be
circular, elliptical, annular, triangular, quadrilateral,
diamond, square, rectangular, trapezoidal, hexagonal,
pentagonal, corrugated, hollow or any other geometric
10   shape. The selected shape will be transferred to the
powder extrudate during the extrusion process and
typically will not vary over the length of the extrudate.
Since the orifice of the extruder is typically a circle,
the extruded green body is typically a cylinder. In the
15   preferred embodiment of the present invention, the
extruder is a either a piston extruder or a twin screw
extruder although other types of extrusion equipment can
be suitably used. The diameter of the extruded green
body, i.e., the longest distance measured across the face
20   of the orifice, is typically between about 1 to 1000
microns, preferably between about 1 and about 20 microns,
more preferably between 1 and 5 microns. The length of
the extruded body is typically between about 10 and about
10,000 microns, preferably between about 1.0 and about
25   5.0 microns. These extruded green bodies typically have
densities in the range of 1.5 to 2.0 g/cm^3.

        In yet another embodiment, the spray dried powder
formulation is cold isostatically pressed ("CIPed") to
produce green billets or bricks. Typically, this is
30   performed at a pressure of between about 10,000 and about
50,000 psi, preferably about 30,000 psi. These billets
may assume any shape but commonly take the form of
rectangles or squares. In preferred embodiments of the
invention, an ISOMAX-30 cold isostatic press,
35   manufactured by National Forge Co. of Irvine, PA is used.
Typically, the CIPed green body has a width of between
about 7.5 cm and about 15 cm, a length of between about

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7.5 cm and about 15 cm, a depth of between about 1.0 and
about 4.0 cm, and a density in the range of 1.5 to 2.0
g/cm.

5   In some embodiments of the present invention, the
green bodies are crushed then sintered. This sequence of
processing produces a controlled textured surface on each
sintered grain. This textured grain provides for
superior grain-matrix bonding, superior abrasive wheel
strength, hardness and toughness and hence superior
10   grinding performance where abrasive-matrix adhesion is
important. In one preferred embodiment of the present
invention, the formulation of the present invention is
extruded to produce a green extrudate, then the extrudate
is crushed, and then sintered. In another preferred
15   embodiment, the formulation is cold pressed to produce
tiles, the tiles are then crushed then sintered. In yet
another embodiment, the formulation is agglomerated to
form pellets which are then crushed and sintered.

       In some embodiments of the present invention, the
20   green bodies are sintered then crushed. This sequence of
processing produces a grain having a smooth surface
texture. In one preferred embodiment of the present
invention, the formulation of the present invention is
extruded to produce a green extrudate which is sintered
25   and then crushed. In another preferred embodiment, the
formulation is cold pressed to produce tiles. The tiles
are then sintered and crushed. In yet another
embodiment, the formulation is agglomerated to form
pellets which are then sintered and crushed.

30   The crushing step of the present invention breaks
down the green or sintered intermediate shaped bodies of
the present invention into polycrystalline grain shapes
of suitable grit sizing and shape for a variety of
abrasive applications. It can be performed by any
35   conventional crushing machine, including, but not limited
to, jaw crushers, impact mills, jet mills, roll mills and
rod mills. In a preferred embodiment for producing

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sharp, high aspect ratio shaped grains, the shaped bodies
are crushed into grains by an 8" by 5" laboratory roll
crusher, manufactured by Sturtevant Co. in Boston, MA.
However, in a preferred embodiment for producing grains
5   of a predetermined cross sectional shape, where the
crushing step is typically limited to fracturing the
shaped body at a predetermined length in order to produce
a uniform aspect ratio, the fracturing of grains having
predetermined cross sectional shapes is commonly
10   performed with an impact mill.

The crushing of the shaped bodies typically results
in polycrystalline silicon carbide grains of either
highly irregular shapes or predetermined cross sectional
shapes. Each grain, however, can be characterized by a
15   length and a diameter. The length of the grain is
defined as the longest straight-line distance present in
the grain while the diameter is defined as the longest
straight line distance perpendicular to the "length" axis
of the grain. The ratio of the length to the diameter of
20   any particular grain is known as the "aspect ratio" of
the grain. Grains having an aspect ratio greater than
about 1.5 are referred to as "weak" shaped grains.
Grains having an aspect ratio of less than about 1.5 are
known as "blocky" shaped grains while grains having an
25   aspect ratio of between about 1.0 and about 1.2 are known
as "strong" shaped grains.

The sintering cycles of the present invention
promote the development of a desirable microcrystalline
grain structure without excessive grain coarsening. Such
30   sintering can be performed by any conventional sintering
means, including hot pressing, pressureless sintering,
gas pressure sintering, hot isostatic pressing (HIP) and
sinter-HIPing. In one embodiment of the present
invention, the formulation is fed directly into a hot
35   press, thus bypassing the formation of a green body.
When hot pressing is used as the sintering method, the
green body is typically sintered at 2100°C for 30 minutes

at 3000 psi ram pressure. When pressureless sintering is
used, heating the green grain to 1500°C under vacuum,
backfilling with argon gas at 1500°C, heating to a
sintering temperature of 2150°C under an argon atmosphere
5   and holding at 2150°C for 15 to 60 minutes in an argon
atmosphere is the preferred firing cycle. When gas
pressure sintering is used, the green body is commonly
soaked at 2100°C for 30 minutes under 3000 psi of argon
gas. The preferred hot isostatic pressing method
10 involves sub-jecting the green body to 2100°C for 15 to
60 minutes at a minimum pressure of 3000 psi under argon.
Final density, hardness, strength and crystallite size in
the sintered grain is influenced by the sintering
temperature and time at temperature in the firing cycle.
15 Typically, grain density, hardness and strength increase
with increased sintering temperature. Crystallite size
in the sintered grain is controlled by the elapsed time
at sintering temperature, where increasing the sintering
time typically produces coarser crystallites.
20   In some processes of the present invention, there is
provided a process for sintering a silicon carbide blend
which has either a moisture content of at least about 0.2
w/o or has an oxygen content of at least about 0.1 w/o,
wherein the sintering cycle comprises a first step which
25 drives off moisture, processing additives, organics and
the like and a second step which drives off oxygen bound
to silicon such as silica and silicates. In preferred
embodiments, this process comprises the steps of:
        a) evacuating a furnace containing a sinterable
30   silicon carbide green body having either a moisture
            content of at least about 0.2 w/o or an oxygen
            content of at least about 0.1 w/o to a vacuum of at
            least about 100 torr, more preferably less than
            about 1 torr,
35   b) heating the green body under vacuum to a
            temperature between about 1000°C and about 1500°,
            c) maintaining the temperature between about 1000°C

and about 1500°C for at least 30 minutes under
vacuum,

d) backfilling the furnace with argon gas to
atmospheric pressure,

5   e) further heating the green body in an argon
atmosphere to a temperature between 2000°C and
2200°C,

f) maintaining the temperature of between 2000°C and
2200°C for at least 15 minutes in an argon

10   atmosphere, and

g) cooling the furnace to room temperature to
produce a sintered ceramic.

As mentioned above, when a green body of the present
invention is crushed then sintered, a textured grain

15   surface results. This texture of the sintered grain, can
be evaluated by comparing either changes in mean surface
roughness (R_a) or surface area due to a change in
topography with a given grit size. When surface
roughness is used for characterizing texture, a grain

20   having a mean roughness of greater than 20 um is
considered to have a coarse surface texture. When mean
roughness is between 10 and 20 um, the grain is
considered to have a moderate texture. When the mean
roughness is between 2 to 10 um, the grain is considered

25   to have a fine texture. When the mean surface roughness
is below 2 um, the grain is considered to have a smooth,
untextured surface. See Figures 1-3, wherein an example
of a fine, moderate and coarse textured sintered abrasive
grains of the present invention, respectively, are set

30   forth at 500X magnification.

The product produced by the present invention is a
sintered, polycrystalline silicon carbide abrasive grain
which contains essentially no free silicon. When the
product is produced by an extrusion process, the product

35   is called an extruded grain. The size of the crystals in
extruded grains typically range from less than one micron
to one millimeter. The grain diameter can be controlled

over a range from 10 to 5000 microns, preferably between
about 100 and about 1000 microns. The extruded grain
aspect ratio typically ranges from between about 1.0 and
1,000, preferably between about 1.0 and about 5.0. The
5   density of extruded grains commonly ranges from about 88%
to about 96% of theoretical density, while its
indentation hardness typically ranges between about 18
and about 27 GPa.

When the product is produced by the hot press
10 method, the product is called a hot-pressed grain. These
grains may take on weak, strong or blocky shapes,
depending on the preferred shape for the intended
application. Because the hot pressed grain is typically
crushed after sintering, its surface generally has a
15 smooth texture. The density of the hot pressed grains is
typically between about 97% and about 99% of theoretical
density, while its hardness typically ranges between 20
to 29 GPa.

When the green body of the present invention is cold
20 iso-statically pressed, the sintered grain is referred to
as a cold pressed sintered grain. The crystallite size
of these grains may be between 1 micron and 1 millimeter.
Their densities range from between about 95% to about 99%
of theoretical density, while hard-ness is usually
25 between about 19 and about 26 GPa. The shape of these
grains can be controlled by the crushing operation to
provide weak, strong or blocky material. When the green
body of this em-bodiment is crushed before sintering, the
resulting surface is highly textured. When the green
30 body is sintered prior to crushing, the surface has a
smooth texture.

When the green body of the present invention is
agglomerated, the sintered grain is referred to as a
pelletized grain. The shape and size of the crushed
35 pelletized grain is typically similar to that of the cold
pressed grain. It may have either a textured or smooth
surface, depending upon the sequence of the sintering and

crushing operations. Its density is typically between
about 95% and about 98% of theoretical density and
hardness is usually between 19 to 25 GPa.

Typically, the sintered silicon carbide ceramic
5   produced from the formulations of the present invention
will have boron present in an amount between about 0.1
and about 30 w/o and excess carbon present in an amount
of between about 0.1 and about 10 w/o. Ceramics sintered
from formulations having higher amounts of sintering aid
10   will comprise between about 4 and about 30 w/o boron,
preferably between about 4 and about 10 w/o, more
preferably between about 4 and about 6 w/o; and between
about 6 w/o and about 10 w/o excess carbon, preferably
between about 6 w/o and about 8 w/o, more preferably
15   between about 6 w/o and about 7 w/o. "Excess carbon" is
defined as the amount of carbon not combined with
compounds containing boron as boron carbide or silicon as
silicon carbide. In preferred embodiments, these
sintered ceramics have a density of at least about 3.00
20   g/cm^3. In more preferred embodiments, at least about 50
w/o of the silicon carbide is in the alpha phase and most
preferably, at least about 75 w/o of the silicon carbide
is in the alpha phase.

The sintered, polycrystalline SiC abrasive grains
25   which have essentially no free silicon can be
incorporated into many abrasive articles either alone, as
a direct substitute for conventional monocrystal SiC
grains, or in combination with conventional SiC grains or
grains of other material compositions. For example, the
30   grains of the present invention can be used as a loose
grit or a lapping compound or can be incorporated into
conventional abrasive, coated abrasive articles, or wear
articles such as vitrified, resinoid or metallic grinding
wheels or stones, coated papers or fabrics, seals or
35   other shaped abrasive products using the same methods
used by the art for attaching or incorporating
monocrystalline SiC grains in abrasive articles. The

grains of the present invention can be manufactured in
any grit size, although typically between the range of an
ANSI 4 grit to a FEPA P1200 grit, with weak, blocky or
strong shapes in a variety of surface textures, ranging
5   from coarse to smooth. The abrasive articles having the
grains of the present invention can then be used in the
same manner as those articles having conventional
monocrystalline SiC grains.

The sintered, polycrystalline silicon carbide
10   abrasive grains which have essentially no free silicon
can be incorporated into many ceramic, metal, organic
polymer or glass matrices as a filler or reinforcement to
form composites. The grains of the present invention may
be incorporated into such matrices either alone, as a
15   direct substitute for conventional monocrystalline SiC
grains, or in combination with conventional grains or
fibers of silicon carbide or other material compositions.
Composite articles made with grains of the present
invention have applications in either abrasive and wear
20   products or structural components where improved
hardness, stiffness, strength, wear resistance, thermal
conductivity, thermal stability, chemical resistance or
friction properties are required.

In order to compare the properties of sintered,
25   polycrystalline silicon carbide grains of the present
invention with those of conventional monocrystalline
silicon carbide grains, grain characterization testing
was performed on individual grain examples. Grain
densities, crystallite size and mechanical properties
30   such as grain friability, impact toughness, indentation
toughness, hardness and compressive strength were
selected as the appropriate measures for comparison. The
test methods utilized for determining these properties
are described below.

35   Grain friability is measured with a DeBeers Mark IV
Friatester provided by DeBeers Industrial Diamond
Division. A review of this equipment and the test method

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is provided in <u>Industrial Diamond Review</u>, March 1974, pp.
133-137. A 20 gram grain sample is prescreened on a
Rotap sieve shaker for 15 minutes using 50 and 60 mesh
electroformed sieves, equivalent to 322 um and 255 um

5   openings. Approximately 0.36 grams of screened material
is then placed in a cylindrical sample capsule together
with a 5/16 inch ball. The capsule and ball are
·fabricated from hardened tool steel. The cycle frequency
is set to 240±3 cpm and the sample capsule is subjected

10   to two dimensional oscillations for a fixed number of
cycles. Separate samples are run at a fixed number of
cycles ranging from 200 to 500. After cycling is
completed, the sample is removed and screened on a Rotap
shaker for 3 minutes using 60 mesh and 70 mesh

15   electroformed sieves, equivalent to 255 um and 213 um
openings. The sample sieve fractions are weighed and the
weight percent of the starting sample which is retained
on the 60 mesh sieve is determined. For each material,
results are reported as either cycle half life, where the

20   number of cycles for 50% retention is determined or a
cumulative rating is assigned based on the sample
retention for a series of fixed cycles.

        Triple impact toughness is measured on a modified
impact mill using a technique developed at Norton Co.

25   The test equipment consists of a conventional impact mill
equipped with variable speed rotating paddles with vacuum
seals and vacuum port so that the mill chamber can be
evacuated to pressure of 0.5 torr with a roughing pump.
Grain samples are prescreened to a nominal 35 to 40 grit

30   sizing. Prior to testing, a sample screen analysis is
performed on a Rotap sieve shaker for 10 minutes. For
the initial test cycle, a nominal sample size of 140
grams is processed in the mill. The mill is sealed and
evacuated. When the chamber pressure reaches 0.5 torr,

35   the paddle motor is activated and rotation is increased
to 3000 rpm. When the paddle speed has stabilized, the
sample is slowly fed into the chamber where it impacts

the paddle blade and rebounds into a sample collection
chamber. After the entire sample is processed, a screen
analysis is repeated on the Rotap and the weight for two
cumulative U.S. screen fractions, -40/+50 and -40/+70,
5   are reported as a fraction of the total sample weight. A
single impact toughness rating, K_1 is obtained from
averaging the weight fraction of fines remaining from the
-50 and -70 sieve fractions. A screened -40/+45 sample
fraction from the first impact cycle is then recycled
10   through the impact mill and a screen analysis is repeated
on the impacted material. The screening results from
this second impact cycle are again analyzed and the
impact toughness is reported as a K_2 value. The process
is repeated a third time with the -40/+45 screen fraction
15   from the second impact cycle and a K_3 impact toughness
value is reported. The K_1 value is generally recognized
as being heavily influenced by grain shape, whereas, the
K_3 value is thought to represent the intrinsic properties
of the grain. In all cases, a lower K value indicates a
20   higher grain impact toughness.

     The compressive strength of spherical or cylindrical
shaped grains was measured by either diametrical
compression (Roark's Formulas for Stress and Strain, 6th
edition, W.C. Young (ed.), McGraw-Hill, New York, 1989,
25   p. 650, or the Brazilian Disk Test (F.Carniero and
A.Barcellos, Union of Testing and Research Laboratories
for Materials and Structures, No. 13 (1953)). Individual
grain samples are placed between two tungsten carbide
flats and the sample is compressed on a Model 4206
30   Instron (Instron Corp. Canton, MA) at a constant cross
head speed of about 0.5 mm/min as a uniaxial compressive
load is applied. The applied load is recorded as a
function of ram displacement until the sample fractures.
The mean maximum compressive stress, strain to failure
35   and compressive modulus is determined for an average of
from ten to twenty five samples.

     Indentation hardness was measured on mounted and

polished grain cross sections with a Vickers indentor and
a Leco DM-400 Microhardness machine, available from Leco
C rp. of St. Louis, Mo., using a 200 gram load.

The indentation fracture toughness of individual
5   grains was measured on mounted and polished grain cross
sections with a Vickers indentor and a Leco DM-400
Microhardness machine using a 500 gram load.

Vitrified grinding wheels were produced which
incorporated the sintered silicon carbide grain as a
10 direct substitute for conventional silicon carbide grain
with no further modification of the wheel formulation.
The wheels comprised between 8 and 9 volume percent of a
high temperature glass bond and 48 volume percent of 46
grit abrasive, the remainder being porosity. A 5 inch
15 o.d., 1.25 inch i.d. by 0.5 inch thick wheel size was
utilized for these tests.

The standard sandblast penetration test was
followed: Approximately 50 cc of round Ottowa sperical
sand, sieved to a -U.S. 24/+ U.S. 30 size fraction, is
20 charged to a small sandblast feed hopper. The sand is
fed through a 3/16 inch i.d. boron carbide nozzle at an
air pressure of 15 psig and feed rate of about 8 cc/sec
so as to impinge on a vitrified test sample. After a six
second sandblast exposure, the surface of the the sample
25 is cleaned with an air blast for 4 seconds and the depth
of surface recession from the penetration of the
sandblast is measured with a dial indicator. The average
of two measurements is reported.

For the MOR (strength) test, a 4.0 inch by 1.0 inch
30 by 0.5 inch thick test bar is placed on a 4 point loading
fixture with a 1 inch top span and a 3 inch bottom span.
The fixture is place on an Model 1125 Instron tester
(Instron Corp., Canton, MA), and the test bar is loaded
at a cross head speed of 0.050 inches/min until failure.
35 Modulus of rupture is calculated from averaging the
maximum load measured at the point of failure for five
test bars.

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For the modulus of elasticity test, a model MK5
Industrial Grindo-Sonic acoustical instrument (J.W.
Lemmens Inc., St. Louis, MO) was utilized for elastic
modulus measurements of test materials. A 4.0 inch by

5   1.0 inch by 0.5 inch thick test bar is supported on a
knife edge fixture with the two knife edges spaced at
points of minimum vibration which are located
approximately 1/5 of the length away from the test bar
ends. An acoustic transducer probe is placed adjacent to

10   the middle of the bar and the sample is tapped lightly
with a nylon hammer. Three measurements are made of the
resonant frequency of the sample. The modulus of
elasticity is calculated from measurement of the sample
dimension, weight, density and frequency, where MOE = $(L^4$

15   $f^2 \cdot$ density) $/ (0.975 \cdot t^2)$.

The grinding performance of vitrified wheels
produced with grains of the present invention was
compared with vitrified wheels produced with conventional
silicon carbide grain in grinding tests on nodular cast

20   iron, titanium and tungsten carbide. Vitrified wheel
grinding tests were performed on a Brown and Sharpe Model
818 surface grinder, available from Brown and Sharp Mfg.
Corp., of North Kingston, RI, using a wheel speed of
4965 rpm equivalent to 6500 sfpm. A workpiece table

25   translation speed of either 30 ft/min or 50 ft/min was
utilized. A 5% aqueous solution of Trim Clear rust
inhibitor (Master Chemical Corp., Perrysburg, OH) was
used in wet grinding tests.

The performance and effectiveness of an abrasive

30   article is typically evaluated in grinding tests where
the rate of wear of the abrasive material and workpiece,
the power consumption for material removal, the grinding
force, translation speed of the workpiece, rotational
speed of the wheel, and workpiece surface finish is

35   measured. Typically, the grinding ratio, or "G-Ratio",
defined as the volumetric ratio of workpiece material
removal to abrasive product wear, is used to characterize

the performance of an abrasive product. The grinding
ratio measures the durability of an abrasive article in
grinding a particular material. Typically, a superior
abrasive article will possess a higher grinding ratio at
5   equivalent or higher workpiece removal rates than an
inferior article. In addition, a superior abrasive
article will maintain a high grinding ratio with
increasing down feed and workpiece removal rates.
Another criterion for characterizing the performance of
10   an abrasive product is workpiece surface finish. A
superior abrasive article will produce a lower surface
roughness on a ground workpiece when compared to an
inferior abrasive article made with an equivalent grit
size.

15   EXAMPLE I
A silicon carbide sinterable formulation was
prepared by mixing 1.18 kg of a phenolic resol resin
(Borden Al-5614), 0.32 kg of boron carbide (Stark HS), 25
kg of deionized water, 0.5 kg of polyethylene glycol
20   (Carbowax 400), 25 kg of silicon carbide powder (Norton
FCP-15) and 5 kg of silicon carbide milling media in a
jar mill. The pH of the mixture was adjusted to 9.0 with
ammonium hydroxide and the formulation was roll milled
for 16 hours. The viscosity and pH of the mixture were
25   measured after milling, and the solids content and pH
were adjusted as necessary prior to spray drying. The
mixture was then spray dried using Niro Type HT portable
spray dryer (Niro Inc., Columbia, MD) to a final moisture
content of between 0.5 to 2.0%. A free-flowing powder
30   was produced from the spray dried formulation which
consisted of spherical aggregates ranging in size between
2 um to 300 um. The resultant spray dried powder
formulation was used as a feed material for Examples I
through V and Examples VII through VIII.
35   Approximately 30 kg of spray dried silicon carbide
powder f rmulation was charged to an Eirich R07 mixer
(Eirich Machines Inc., Maple, Ontario, Canada) equipped

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with a pelletizing rotor blade. 1.125 kg of Goshenol
KH17S PVA (Nippon Gohsei, Osaka, Japan) was added to the
mixer and dry mixed with the powder formulation at low
speed.   With the mill operating at low speed, 5.0 kg of

5   a water-methanol solution (50/50 weight percent) was
aspirated and sprayed onto the solid charge during
mixing. The mill speed was increased and adjusted to
provide for formation of small, uniform spherical pellets
through agglomeration of the powder charge. Typically,

10   pellet sizes ranged between 300 to 2000 um with a peak
distribution between 500 to 1000 um. The pellet density
was between 1.5 to 1.8 g/cm^3.

The green pellets were dried overnight in a
convection oven at 110°C prior to firing. The pellets

15   were subsequently pressureless sintered as follows.
Green pellets were heated at a rate of 15°C per minute to
1500°C under a vacuum ranging from less than 0.001 torr
to 100 torr. After holding at 1500°C for 30 minutes
under vacuum, the furnace was backfilled with argon gas

20   to a nominal pressure of 760 torr. The temperature was
then increased at a rate of 20°C per minute to 2150°C and
held for one hour. After cooling to room temperature,
pellet densities were measured by the Archimedes method,
by helium pycnometry and by mercury intrusion porosimetry

25   and ranged between 3.05 to 3.21 g/cm^3.

Next, sintered pellets were crushed to appropriate
size and shape. An impact mill, equipped with steel
paddles and operating at 1300 rpm, was used to attain
blocky shaped grains. A roll crusher, with a gap setting

30   of approximately twice the average diameter of the
targeted grit size, was used to attain weak shaped
grains. Grit sizing was obtained by screening through
conventional polyester or stainless steel mesh sizes to
either ANSI, FEPA or CAMI standard grit sizes. For small

35   grain batches, an 18 inch Sweco Vibro-energy Separator,
manufactured by Sweco Inc. of Florence, KY, was used for
screening. For large grain batches, a 4 sq. ft. Rotex

screener, manufactured by Rotex Inc. of Cincinnati, OH,
was used.

5   The physical and mechanical properties of the impact
milled, blocky shaped, sintered silicon carbide grain
produced by this method are compared to conventional
silicon carbide grain in Figure 4. The mechanical
properties and grinding performance of vitrified grinding
wheels made with this grain are provided in Figures 5 and
6. The grain properties, wheel properties and grinding
10   performance data set forth in Figures 4-6 were drawn from
blocky grain embodiments of Examples I-IX of the present
invention.

EXAMPLE II

          A sinterable silicon carbide powder formulation was
15   spray dried and pelletized according to the procedure
identified in Example I. The green pellets were dried
overnight in a convection oven at 110°C prior to
crushing. The dried pellets were crushed to appropriate
size using either an impact mill for blocky shaped grain
20   or a roll crusher for weak shaped grain. Grit sizing was
achieved by screening to ANSI, FEPA or CAMI standard grit
sizes using either a Sweco or Rotex screener. The green,
unfired grain was classified to approximately 20%
oversize in order to accommodate the shrinkage which
25   occurs during sintering.

          The green, crushed and classified grain was
subsequently sintered for 1 hour at 2150°C following the
firing cycle of Example I. Fired densities were measured
by the Archimedes method, by helium pycnometry and by
30   mercury intrusion porosimetry and ranged between 3.06 to
3.19 g/cm^3.

          Grains produced by the method of this example
possessed a unique surface texture which has not been
observed in any other abrasive grain material. Figures
35   1-3 shows the range of surface textures of grains
produced by this method where examples of fine, moderate
and coarse surface textures, respectively, are shown at

500 X.

The characteristic properties of grains made with this method are provided in Figure 4. The mechanical properties and grinding performance of vitrified grinding
5   wheels made with this grain are provided in Figures 5 and 6.

EXAMPLE III

A spray dried sinterable powder formulation was produced according to the procedure identified in Example
10 I. Approximately 500 grams of spray dried powder blend was charged to a 6" by 6" square mold and uniaxially pressed at 2000 psi ram pressure. The resultant pressed brick was removed from the mold, sealed in a polyethylene bag and placed in an Isomax-30 cold isostatic press
15 (National Forge Co., Irvine, PA). The die pressed brick was then pressed at 30,000 psi under isostatic conditions to a green density of between 1.6 to 2.0 g/cm^3. The isostatically pressed brick was removed from the polyethylene bag and stored in a drying oven at 110°C.
20   The green bricks were dried overnight at 110°C prior to firing. The bricks were subsequently sintered for 1 hour at 2150°C following the firing cycle of Example I. Fired densities were measured by the Archimedes method, by helium pycnometry and by mercury intrusion porosimetry
25 and ranged between 3.13 to 3.17 g/cm^3.

Sintered bricks were crushed in a jaw crusher to a nominal 1/4" sizing and fed to either an impact mill for "blocky" shaped grain or a roll crusher for "weak" shaped grain. Grit sizing was obtained by screening crushed
30 grain through polyester or stainless steel screens to either ANSI, FEPA or CAMI standard grit sizes using a Sweco screener.

The characteristic properties of grains made with this method are provided in Figure 4. The mechanical
35 properties and grinding performance of vitrified grinding wheels made with this grain are provided in Figures 5 and 6.

EXAMPLE IV

This Example is a prophetic Example. Cold
isostatically pressed powder bricks are processed
according to the procedures of Example III. After drying
5   overnight at 110°C, the bricks are crushed to a nominal
1/4" sizing and fed to either an impact mill for "blocky"
shaped grain or a roll crusher for "weak" shaped grain.
Grit sizing is achieved by screening crushed grain
through ANSI, FEPA or CAMI standard screen mesh sizes
10   using either a Sweco or Rotex screener. The green grain
is classified to approximately 20% oversize in order to
accommodate the shrinkage which occurs during sintering.

The green crushed and classified grain is
subsequently sintered for 1 hour at 2150°C following the
15   firing cycle of Example I. As is observed in Example II
above, grains produced by this example will possess a
unique surface texture which has not been observed in
other abrasive grain materials.

EXAMPLE V

A spray dried sinterable powder formulation was
produced according to the procedure identified in Example
I. Approximately 700 grams of spray dried powder blend
5 was charged to a 6" by 6" graphite hot press mold cavity.
The powder was tamped for improved packing and covered
with a graphite spacer. A total of nine successive
layers of powder and mold spacers were placed in the mold
cavity. The mold assembly was placed in a uniaxial press
10 and pressed at 300 psi for compaction at room
temperature. Additional powder was charged as was needed
to the mold cavity and the mold assembly was compacted
again at 300 psi.

The mold assembly was placed in a vacuum hot press
15 furnace, approximately 300 psi ram pressure was applied
to the mold, and the furnace was evacuated, backfilled
with argon and re-evacuated at room temperature. The
furnace was then heated to 1800°C as the ram pressure was
increased from 300 psi to 3000 psi. The ram pressure was
20 held constant at 3000 psi as the temperature was raised
to 2075°C. The furnace was held at 2075°C for 30 minutes
at which time the power was turned off and the furnace
was cooled to room temperature.

The hot pressed plates were crushed in a jaw crusher
25 to a nominal 1/4" sizing and fed to either an impact mill
for "blocky" shaped grain or a roll crusher for "weak"
shaped grain. Grit sizing was obtained by screening
crushed grain through polyester or stainless steel
screens to either ANSI, FEPA or CAMI standard grit sizes
30 using a Sweco screener.

The characteristic properties of grains made with
this method are provided in Figure 4. The mechanical
properties and grinding performance of vitrified grinding
wheels made with this grain are provided in Figures 5 and
35 6.

EXAMPLE VI

A silicon carbide sinterable formulation was

prepared by mixing 6.5 kg of sub-micron silicon carbide
powder (Norton FCP-15), 6.5 kg of 2-3 micron silicon
carbide powder (Norton E277), 0.13 kg of Black Pearls
1300 carbon black (Cabot Corp., Billerica, MA), 0.13 kg

5   of BO-250 amorphous boron powder (Atlantic Equipment
Engineers, Bergenfield, NJ) and 6.5 kg of deionized water
in a jar mill for 72 hours. The mill batch was then
freeze dried using a Unitop 200/Freezemobile 6 laboratory
frieze drier (The Virtis Co., Gardiner, NY). The dried

10   formulation was crushed and sieved through a U.S. 80 mesh
screen prior to use.

An extrusion formulation was prepared by mixing 9 kg
of the frieze dried powder blend, 0.138 grams of Methocel
A4M (Dow Chemical Co., Midland, MI), 180 grams of

15   Sorbitol (Lonza Inc., Fair Lawn, NJ) and 1.94 kg of
distilled water in a sigma blade mixer. The mixture was
kneaded for approximately 2 hours in an Abbe MP sigma-
blade mixer (Paul O. Abbe Inc., Little Falls, NJ) to
produce an extrudable mix consistency.

20   This formulation was then extruded with a piston
extruder equipped with a 20RT electo-plated perforated
plate die (Stork Veco International, Bedford, MA). This
die had a nominal thickness of 0.018 inches, an 8% open
area and hole sizing of 0.012 inches. The extrusion

25   formulation was placed in the extruder bore and pre-
compressed under vacuum for degassing the mix. During
extrusion, the piston ram pressure was adjusted between
500 to 5000 psi. The extrudate was dried overnight at
140°C and was then partially crushed to increase bulk

30   density prior to firing.

The dried extrudate was then sintered at 2150°C for
1 hour following the firing cycle of Example I. The
fired density was measured using both Archimedes method
and helium pycnometry and ranged between 3.05 to 3.19

35   g/cm^3. The sintered extrudate was fractured on an impact
mill equipped with steel paddles rotating between 350 to
500 rpm in order to produce cylindrical-shaped grain with

a controlled aspect ratio.. The fractured extrudate was classified to a nominal aspect ratio f 2.0 taking a -US 35/+US 100 fraction screened with an 18 inch Sweco Vibro Energy Separator.

5   The characteristic properties of grains made with this method are provided in Figure 4. The mechanical properties and grinding performance of vitrified grinding wheels made with this grain are provided in Figures 5 and 6.

10   EXAMPLE VII
       A spray dried sinterable powder formulation was produced according to the procedure identified in Example I. An extrudable formulation was prepared from 1 kg of this powder blend which was mixed in a jar roll mill

15   overnight with 10 grams of laboratory grade stearic acid (Sargeant-Welch Scientific Co., Skokie, IL), 20 grams of Goshenol KH17S PVA, 10 grams of Sorbitol and 480 grams of distilled water. The mixture was dried at 150°C overnight, then crushed and screened through a U.S. 80

20   mesh sieve.
       Approximately 90 grams of the dried extrusion mixture was charged to a 3" by 3" square mold and tiles were uniaxially pressed at 2000 psi ram pressure. The resultant pressed tiles were removed from the mold,

25   sealed in a polyethylene bag and placed in a cold isostatic press. The die pressed tiles were then pressed at 30,000 psi under isostatic conditions to a green density of between 1.6 to 1.8 g/cm^3. The isostatically pressed tiles were removed from the polyethylene bag and

30   stored in a drying oven at 110°C overnight. The tiles were subsequently sintered for 1 hour at 2150°C following the firing cycle of Example I. Fired densities were measured by the Archimedes method and ranged between 3.12 to 3.16 g/cm^3.

35   Samples of the extrudable mixture were prepared for extrusion and measurement of mix rheology. Approximately 90 grams of a sinterable silicon carbide formulation '

prepared according to the method identified in Example I
was mixed with 0.9 grams of stearic acid, 1.8 grams of
Goshenol K17S PVA, 0.9 grams of Sorbitol and 18 grams of
distilled water in a Brabender Plasti-Corder (Brabender

5   Instruments Inc., South Hackensack, NJ) equipped with a
sigma-blade mixing head. Samples of this mix were
extruded through both 0.0826 inch diameter and 0.0144
inch diameter orifices using a Kayness Galaxy IV
capillary rheometer (Kayness Inc., Honeybrook, PA). The

10   extrudate was dried overnight at 150°C prior to
sintering. The dried extrudate was sintered at 2150°C
for 1 hour following the firing cycle of Example I. The
fired density was measured using both Archimedes method
and helium pycnometry and ranged between 3.05 to 3.21

15   g/cm^3.

EXAMPLE VIII

A sinterable powder slurry formulation was produced
according to the procedure identified in Example I. A
nominal 50% solids slurry was processed in a Niro HT

20   spray drier using a 50 mm AR centrifugal atomizer wheel
operated at 40,000 rpm. The inlet drying air temperature
was set at 280°C with a flowrate of 70 kg/hr. The outlet
air temperature was maintained between 90°C and 100°C and
the powder slurry was dried to a moisture content of

25   between 0.88 and 1.35% at a throughput rate of
approximately 10 kg/hr. The resultant product consisted
of green spherical aggregates with a mean diameter, or d_{50},
of approximately 25 um. The mean powder aggregate size
and d_{50} was controlled over the range of 10 um to 60 um

30   through adjustment of the slurry viscosity, solids
loading or rotation speed of the atomizing wheel.

The remainder of this Example is a prophetic
Example. The green atomized powder aggregates are
sintered at 2150°C for 1 hour following the firing cycle

35   of Example I. The sintered aggregates are jet milled for
crushing to final size and shape and the processed
material is then classified by either a sedimentation

method or air classification to grain sizes which range
between FEPA P240 to P1200 microgrit standards.

<div align="center">EXAMPLE IX</div>

A silicon carbide sinterable formulation was
5   prepared by mixing 1.43 kg of a phenolic resol resin
(Borden Al-5614), 0.51 kg of boron carbide (Stark HS), 10
kg of deionized water, 0.2 kg of polyethylene glycol
(Carbowax 400), 10 kg of silicon carbide powder (Norton
FCP-15) and approximately 2 kg of silicon carbide milling
10   media in a jar mill. The pH of the mixture was adjusted
to 9.0 with ammonium hydroxide and the formulation was
roll milled for 16 hours. The viscosity and pH of the
mixture were measured after milling, and the solids
content and pH were adjusted as necessary prior to spray
15   drying. The mixture was then spray dried using a Niro
Type HT portable spray dryer (Niro Inc., Columbia, MD) to
a final moisture content of between 0.5 to 2.0%. A free-
flowing powder was produced from the spray dried
formulation which consisted of spherical aggregates
20   ranging in size between 2 um to 300 um. The resultant
spray dried powder formulation was used as a feed
material for this example.

Approximately 10 kg of spray dried silicon
carbide powder formulation was charged to an 20 liter
25   Lödige horizontal mixer (Little Bros. Inc., Florence, KY)
equipped with a pelletizing rotor blade. Approximately
0.375 kg of Goshenol KH17S PVA was added to the mixer and
dry mixed with the powder formulation at low speed. With
the mill operating at low speed, approximately 2.5 kg of
30   a water-methanol solution (50/50) was aspirated and
sprayed onto the powder charge during mixing. The mill
speed was increased and adjusted to provide for formation
of small, uniform spherical pellets through agglomeration
of the wet powder. Typically, pellet sizes ranged
35   between 300 to 5000 um with a peak distribution between
1000 to 3000 um. The pellet density was between 1.5 to
1.8 g/cm^3.

<div align="center">30</div>

The green pellets were dried overnight in a
convection oven at 110°C prior t firing. The pellets
were subsequently presureless sintered at 2150°C for 1
hour following the firing cycle of Example I. Pellet
5   densities were measured by the Archimedes method, by
helium pycnometry and by mercury intrusion porosimetry
and ranged between 3.05 to 3.21 g/cm³. Sintered pellets
were crushed to appropriate size for testing using a
Sturtevant laboratory roll mill. Sizing to 46 Grit was
10 obtained on a Model B, Ro-Tap Testing Sieve Shaker
(W.S.Tyler Inc., Gastonia, NY) equipped with U.S.
screens. Indentation toughness, Vickers indentation
hardness and DeBeers friability tests were performed on
grain samples and the results are reported in Figure 4.
15   COMPARATIVE EXAMPLES
    In order to compare the grains of the present
invention to those of the prior art, two types of
conventional silicon carbide grains, green CRYSTOLON 39C
manufactured by Norton A/S in Lillesand, Norway, and
20 black CRYSTOLON 37C grains manufactured by Norton Company
of Worcester, Massachusetts, were tested in the same
manner as the above examples. The characteristic
properties of these grains are provided in Figure 4.
    As set forth in Figure 4, the results of grain
25 characterization tests indicate that the grains of the
present invention exhibit superior properties as compared
to the prior art. Comparing the comparative examples to
the embodiments of the present invention reveals that
grains of the present invention display superior
30 hardness, toughness, compressive strength and modulus.
    The mechanical properties of vitrified grinding
wheels made with the grains of the Comparative Examples
are provided in Figure 5. In comparing the mechanical
properties of vitrified wheel materials made from the
35 comparative examples with the embodiments of the present
invention, vitrified composite materials of the present
invention display superior wear resistance (hardness);

strength (modulus of rupture), and modulus of elasticity.

The grinding performance of vitrified grinding wheels made with the grains of the Comparative Examples are provided in Figure 6. Comparing grinding test
5   results of the comparative examples to the embodiments of the present invention reveals that the present invention displays superior grinding ratios, metal removal rates and workpiece surface finish. In particular, the abrasive articles having sintered, shaped polycrystalline SiC
10   grains of the present invention typically have grinding ratios significantly higher than abrasive articles made from conventional monocrystalline SiC grains, thus indicating high durability. In addition, as shown by the data of Figure 6, abrasive articles having grains of the
15   present invention maintain high grinding ratios at increased cutting rates. Further, the workpiece surface finish obtained with abrasive articles containing grains of the present invention is also superior to the finish obtained with conventional SiC grains. These grinding
20   results demonstrate very clearly that the performance of sintered, shaped polycrystalline SiC grains of the present invention is superior to that of conventional monocrystalline SiC grains.

The results reported above indicate that the grains
25   of the present invention exhibit substantially superior performance over conventional silicon carbide grains in abrasive applications. Without wishing to be tied to a theory, it is believed that the superior performance can be attributed to the microcrystalline structure and shape
30   of the sintered polycrystalline grains as well as the absence of inclusions and intrinsic defects such as cracks or dislocations. In particular, the microcrystalline nature of the grains should provide an intrinsically tougher grain than the prior art alpha-SiC
35   monocrystal grain since intergranular fracture and crack propagation proceed less easily in a polycrystalline grain than transgranular fracture and crack propagation

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in a mono-crystalline grain. Furthermore, in
consideration of the unique surface texture which is
provided with abrasive grains produced by the method of.
the present invention, it is believed that the superior

5   mechanical properties and grinding performance in an
abrasive article can be attributed to an improved bonding
of the grain to the matrix phase which produces an
abrasive article with improved strength, stiffness,
hardness and wear resistance.

I Claim:

1.   A sintered, polycrystalline silicon carbide abrasive grain having essentially no free silicon.

2.   The grain of claim 1 having an indentation fracture toughness of at least 2.0 MPa.m$^{1/2}$.

3.   The grain of claim 2 having an indentation fracture toughness of at least 2.5 MPa.m$^{1/2}$.

4.   The grain of claim 1 having a compressive strength of at least about 15,000 psi.

5.   The grain of claim 1 having a compressive strength of at least about 20,000 psi.

6.   The grain of claim 1 having a compressive strength of at least about 75,000 psi.

7.   The grain of claim 1 having a compressive modulus of at least about 5×10^6 psi.

8.   The grain of claim 1 having a compressive modulus of at least about 6×10^6 psi.

9.   The grain of claim 1 having a density of at least about 3.0 g/cm^3.

10.   The grain of claim 1 having an 200 g indentation hardness of at least about 25 GPa.

11.   The grain of claim 1 having a K_1 triple impact toughness of less than about 0.80.

12.   The grain of claim 1 having a K_1 triple impact toughness of less than about 0.50.

13.   The grain of claim 1 having a K_1 triple impact toughness of less than about 0.26.

14.   The grain of claim 1 having a K_2 triple impact toughness of less than about 0.60.

15.   The grain of claim 1 having a K_2 triple impact toughness of less than about 0.40.

16.   The grain of claim 1 having a K_2 triple impact toughness of less than about 0.20.

17.   The grain of claim 1 having a K_3 triple impact toughness of less than about 0.60.

18.   The grain f claim 1 having a K_3 triple impact toughness of less than about 0.40.

19. The grain of claim 1 having a K_3 triple impact
     toughness of less than about 0.21.

20. The grain of claim 1, wherein the mean diameter of
     the crystallites is between about 1 micron and about

5   1000 microns.

21. The grain of claim 1, wherein the mean diameter of
     the crystallites is between about 1 micron and about
     20 microns.

22. The grain of claim 1, wherein the mean diameter of

10   the crystallites is between about 1 micron and about
     5 microns.

23. The grain of claim 1 having a mean surface roughness
     of less than about 2 microns.

24. The grain of claim 1 having a mean surface roughness

15   of between about 2 and about 10 microns.

25. The grain of claim 1 having a mean surface roughness
     of between about 10 and about 20 microns.

26. The grain of claim 1 having a mean surface roughness
     of more than about 20 microns.

20 27. The grain of claim 1 wherein the grain has a shape
     that is weak.

28. The grain of claim 1 wherein the grain has a shape
     that is strong.

29. The grain of claim 1 wherein the grain has a

25   predetermined cross sectional shape which does not
     vary over its length.

30. The grain of claim 29 where the predetermined cross
     sectional shape is circular, annular, elliptical,
     triangular, quadrilateral, diamond, square,

30   rectangular, trapezoidal, hexagonal, pentagonal,
     corrugated or hollow.

31. The grain of claim 29 wherein the grain has an
     aspect ratio of between about 1.0 and about 5.

32. The grain of claim 1 wherein the grain comprises

35   excess carbon.

33. The grain of claim 32, wherein the excess carbon is
     present of between about 0.1 and about 10.0 weight

percent.

34. The grain of claim 1, wherein the grain comprises boron.

35. The grain of claim 34, wherein the boron is present of between about 0.1 and about 30 weight percent.

36. The grain of claim 1 comprising a sintering aid selected from the group consisting of CaO, MgO, BaO, alkaline earth oxides, transition metal oxides, rare earth oxides, alumina, silica, phosphate compounds, borate compounds, metals, metal carbides, borides, aluminides, silicides, and phosphides.

37. A process for producing a textured, sintered, polycrystalline silicon carbide abrasive grain having essentially no free silicon, comprising the sequential steps of:

a) forming a shape from a formulation comprising silicon carbide powder and at least one sintering aid,

b) crushing the shape to produce non-spherical silicon carbide grains, and

c) sintering the non-spherical silicon carbide grains in the absence of free silicon.

38. The process of claim 37, wherein the shape is formed by agglomeration.

39. The process of claim 37, wherein the shape is formed by extrusion.

40. The process of claim 37, wherein the shape is formed by cold isostatic pressing.

41. The process of claim 37, wherein the shape is formed by injection molding.

42. The process of claim 37, wherein the shape is formed by slip casting.

43. The process of claim 37, wherein the shape is formed by tape casting.

44. A process for producing a sintered, polycrystalline silicon carbide abrasive grain having essentially no free silicon, comprising the sequential steps of:

a) forming a shape from a formulation comprising
silicon carbide powder and at least one sintering
aid,

b) sintering the shape in the absence of free

5   silicon, and

c) crushing the shape to produce non-spherical
silicon carbide grains.

45. The process of claim 44, wherein the shape is formed
by agglomeration.

10   46. The process of claim 44, wherein the shape is formed
by extrusion.

47. The process of claim 44, wherein the shape is formed
by cold isostatic pressing.

48. The process of claim 44, wherein the shape is formed
15   by injection molding.

49. The process of claim 44, wherein the shape is formed
by slip casting.

50. The process of claim 44, wherein the shape is formed
by tape casting.

20   51. The process of claim 44, wherein the shape is formed
by hot pressing.

52. An abrasive product comprising the abrasive grain of
claim 1.

53. The abrasive product of claim 52 comprising a
25   grinding wheel.

54. A silicon carbide grinding wheel having a standard
sandblast penetration of less than about 2.5 mm.

55. The grinding wheel of claim 54 having a sandblast
penetration of less than about 2.0 mm.

30   56. The grinding wheel of claim 54 having a sandblast
penetration of less than about 1.0 mm.

57. A silicon carbide grinding wheel having an MOR
strength of at least about 1850 MPa.

58. The silicon carbide grinding wheel of claim 57
having an MOR strength of at least about 2000 MPa.

5 59. The grinding wheel of claim 57 having an MOR
strength of at least about 2500 MPa.

60. A silicon carbide grinding wheel having a bond
content of about 9% and grinding ratio of at least
about 0.5, when wet grinding titanium at a downfeed

10   of 0.3 mils.

61. The grinding wheel of claim 60 having a metal
removal rate of at least about 0.002 in^3/min.

62. The grinding wheel of claim 60 having a metal
removal rate of at least about 0.003 in^3/min.

15 63. A silicon carbide grinding wheel having a bond
content of about 9% and a grinding ratio of at least
about 20 when dry grinding nodular iron having a
Rockwell B hardness of between about 110 and 113 at
a downfeed of about 2.0 mils.

20 64. The grinding wheel of claim 63 having a metal
removal rate of at least about 0.045 in^3/min.

65. The grinding wheel of claim 63 having a surface
finish having a mean roughness of less than about
150 microinches.

25 66. A silicon carbide grinding wheel having a bond
content of about 9% and a grinding ratio of at least
about 150 when dry grinding nodular iron having a
Rockwell B hardness of between about 110 and 113 at
a downfeed of about 0.5 mils.

67.   The grinding wheel of claim 66 having a metal
removal rate of at least about 0.013 in^3/min.

68.   The grinding wheel f claim 66 having a surface
finish having a mean roughness of less than about 50
microinches.

69.   A coated abrasive article comprising grains of claim
1.

70.   A composite article comprising a matrix and grains
of claim 1.

71.   A composite of claim 70 wherein the matrix comprises
a metal.

72.   A composite of claim 70 wherein the matrix comprises
a ceramic.

73.   A composite of claim 70 wherein the matrix comprises
an organic polymer.

74.   A composite of claim 70 wherein the matrix comprises
a glass.

75.   A sinterable silicon carbide powder formulation
comprising:

a) a sinterable silicon carbide powder having an
average particle size of less than one micron and
present in an amount of from about 60 w/o to about
90 w/o of the formulation,

b) a carbon-based additive present in an amount of
from about 6 w/o to about 10 w/o of the formulation,
and

c) a boron-based additive present in an amount of
from about 4 w/o to about 30 w/o of the formulation.

76.   The formulation of claim 75, where the carbon-based
additive is present in an amount of from about 6 w/o
to about 8 w/o of the formulation.

77.   The formulation of claim 75, where the carbon-based
additive is present in an amount of from about 6 w/o
to about 7 w/o of the formulation.

78.   The formulation of claim 75, further comprising a
temporary binder present in an amount of from about
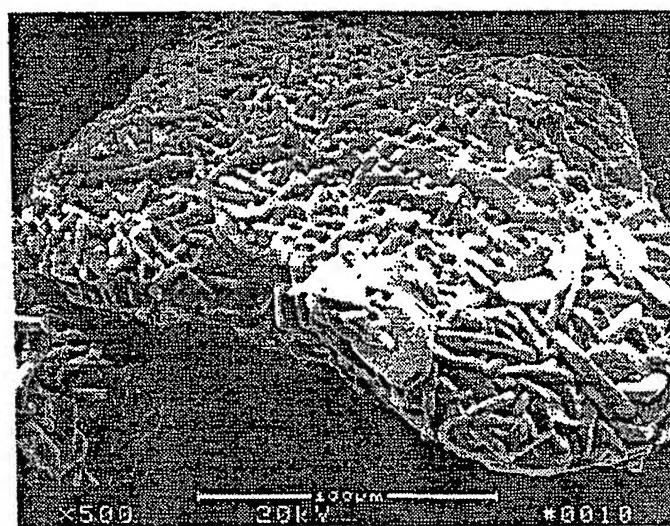0.1 w/o to about 10 w/o of the formulation.

79.   The formulation of claim 75, where the boron-based
      additive is present in an amount of from about 4 w/o
      to about 10 w/o of the formulation.

80.   The formulation of claim 75, where the boron-based
5   additive is present in an amount of from about 4 w/o
      to about 6 w/o of the formulation.

81.   The formulation of claim 75, further comprising a
      temporary binder present in an amount of from about
      0.25 w/o to about 5 w/o of the formulation.

10 82.   A sintered silicon carbide ceramic comprising:
      a) silicon carbide present in an amount of from
      about 60 w/o to about 90 w/o of the ceramic,
      b) excess carbon present in an amount of from about
      6 w/o to about 10 w/o of the ceramic, and
15   c) boron present in an amount of from about 4 w/o to
      about 30 w/o of the ceramic, said ceramic having a
      density of at least about 3.00 g/cm^3.

83.   The ceramic of claim 82, where the excess carbon is
      present in an amount of from about 6 w/o to about 8
20   w/o of the ceramic.

84.   The ceramic of claim 82, where the excess carbon is
      present in an amount of from about 6 w/o to about 7
      w/o of the ceramic.

85.   The ceramic of claim 82, where at least about 50 w/o
25   of the silicon carbide is present as alpha.

86.   The ceramic of claim 82, where the boron is present
      in an amount of from about 4 w/o to about 10 w/o of
      the ceramic.

87.   The ceramic of claim 82, where the boron is present
30   in an amount of from about 4 w/o to about 6 w/o of
      the ceramic.

88.   The ceramic of claim 85, where at least about 75 w/o
      of the silicon carbide is present as alpha.

89.   A process for producing a sintered silicon carbide
35   ceramic comprising the sequential steps of:
      a) milling an aqueous slurry of coarse silicon
      carbide powder at a predetermined pH value of

40

between about 6.0 and about 10.0 to reduce the mean
particle size of the silicon carbide powder to less
than one micron,

b) adding at least one sintering additive to the
aqueous silicon carbide powder slurry,

c) homogeneously mixing the sintering additive with
the aqueous silicon carbide slurry,

d) drying the milled slurry to a moisture content of
less than 30% by weight of the silicon carbide
powder,

e) forming a green body from the dried slurry, and

f) sintering the green body without subjecting the
green body to chemical treatments which remove
oxygen or other impurities.

90. The process of claim 89 wherein the milled slurry is
dried to less than about 2 w/o of the silicon
carbide powder.

91. A process for producing a dense silicon carbide
ceramic comprising the sequential steps of:

a) evacuating a furnace containing a sinterable
silicon carbide green body having either a moisture
content of at least about 0.2 w/o or an oxygen
content of at least about 0.1 w/o to a vacuum of at
least about 100 torr,

b) heating the green body under vacuum to a
temperature between about 1000°C and about 1500°,

c) maintaining the temperature between about 1000°C
and about 1500°C for at least 30 minutes under
vacuum,

d) backfilling the furnace with argon gas to
atmospheric pressure,

e) further heating the green body in an argon
atmosphere to a temperature between 2000°C and
2200°C,

f) maintaining the temperature of between 2000°C and
2200°C for at least 15 minutes in an argon
atmosphere, and

g) cooling the furnace to room temperature.

92.   The pr cess of claim 91 comprising evacuating the
        furnace to less than about 1 torr.
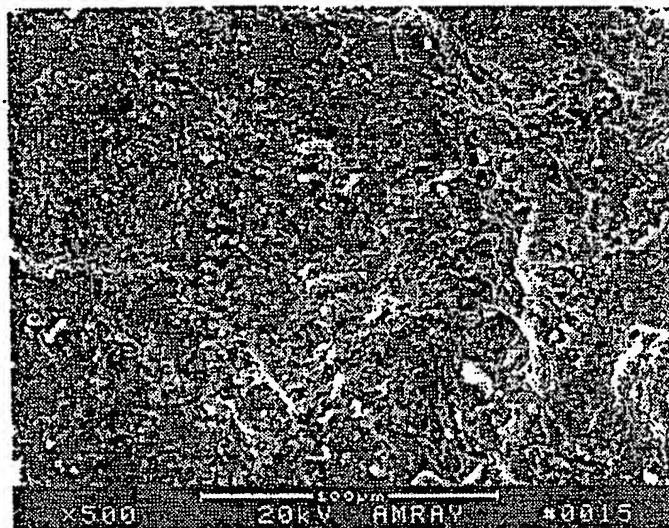
FIG. 1

FIG. 2
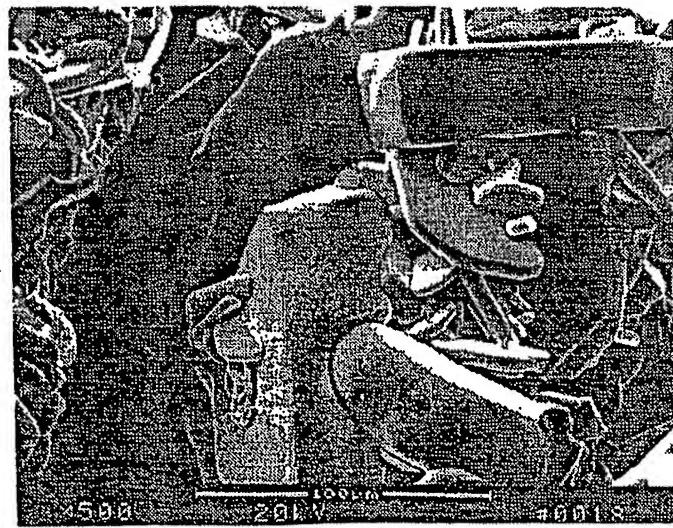
FIG. 3

EXAMPLE	DENSITY (g/cc)			MEAN CRYSTALLITE SIZE (um)	GRAIN FRIABILITY		TRIPLE IMPACT TOUGHNESS			INDENTATION HARDNESS (GPa)	INDENTATION TOUGHNESS (MPa M$^{1/2}$)	COMPRESSIVE STRENGTH (psi)	COMPRESSIVE MODULUS (Msi)
	H$_2$O	He	Hg		YIELD	HALF-LIFE	K$_1$	K$_2$	K$_3$				
I	3.13	3.21	3.18	1-3	247/400	535	0.26	0.20	0.21	25.2	2.73	75,600	6.0
II	3.06	3.19	3.15	3-6	239/400	478	-	-	-	22.1	2.00	-	-
III	3.15	3.17	3.14	2-4	218/400	450	-	-	-	26.4	2.72	-	-
V	3.17	3.19	3.20	1-3	238/400	463	-	-	-	28.0	1.96	-	-
VI	3.18	3.21	-	2-5	-	-	-	-	-	27.4	-	15,000	0.2
IX	3.09	-	-	1-3	208/400	367	-	-	-	23.6	2.13	-	-
39C	3.14	3.21	-	>>1000	236/400	430	1.07	0.84	0.80	20	1.89	7,000	4.0
37C	3.21	3.21	-	>>1000	246/400	462	-	-	-	22.8	1.79	-	-

FIG. 4

EXAMPLES (46 GRIT)	BOND CONTENT (48 V/O ABRASIVE)	SANDBLAST PENETRATION (mm)	MODULUS OF RUPTURE (psi)	ELASTIC MODULUS (Msi)	DENSITY (g/cc)
I	8%	1.53	2223	33.71	1.694
I	9%	0.98	2811	39.94	1.731
II	8%	2.79	1868	25.74	1.650
II	9%	1.99	–	28.5	1.69
III	8%	2.36	2094	31.27	1.660
III	9%	1.95	2517	35.47	1.702
VI	9%	2.08	–	15.6	1.423
39C	8%	3.48	1599	26.87	1.693
39C	9%	3.16	1291	29.15	1.706
37C	8%	3.47	1460	27.66	1.676
37C	9%	2.16	1748	31.50	1.705

FIG. 5

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EXAMPLE (46 GRIT)	BOND CONTENT (%)	DOWN FEED (mils)	AVERAGE PEAK POWER (P)	G-RATIO (G)	METAL REMOVAL RATE (in³/min)	WHEEL WEAR RATE (in³/min)	SURFACE FINISH (in. x 10⁻⁶)
MATERIAL: NODULAR IRON (ROCKWELL B HARDNESS: 110-113), DRY GRINGING							
I	9	0.5	570	187	0.0135	0.00007	42
		1.0	580	268	0.0256	0.00010	55
		2.0	720	182	0.0497	0.00027	99
II	9	0.5	320	174	0.0118	0.00007	63
		1.0	510	186	0.0248	0.00013	82
		1.5	400	110	0.0369	0.00083	90
		2.0	400	29	0.0458	0.00160	130
III	9	0.5	430	153	0.0126	0.00008	47
		1.0	470	179	0.0247	0.00014	63
		2.0	440	87	0.0484	0.00056	108
		2.0	420	40	0.0464	0.00117	130
VI	9	0.5	1040	18	0.0257	0.0014	-
39C	9	0.5	174	111	0.0118	0.00011	69
		1.0	130	4	0.0138	0.00330	110
37C	9	0.5	220	193	0.0126	0.00007	58
		1.0	330	245	0.0240	0.00010	69
		1.5	109	20	0.0328	0.00161	109
		2.0	105	3	0.0240	0.00762	105
III	8	0.5	220	63	0.0119	0.00019	55
		1.0	378	96	0.0242	0.00025	78
		1.5	300	40	0.0349	0.00088	110
		2.0	180	3	0.025	0.00805	109
37C	8	0.5	130	47	0.0113	0.00024	78
		1.0	100	5	0.0147	0.00314	55
MATERIAL: TUNGSTEN CARBIDE (370 CARBOLOY), WET GRINDING							
I	9	0.3	730	0.035	0.0014	0.03984	-
		0.5	760	0.0285	0.0021	0.07343	-
II	9	0.3	480	0.0188	0.0009	0.04721	-
		0.5	520	0.0093	0.0008	0.08191	-
III	9	0.3	480	0.0076	0.0004	0.04931	-
		0.5	550	0.0089	0.0007	0.08389	-
VI	9	0.5	1550	24.69	0.2924	0.0118	-
39C	9	0.5	430	2.9	0.1462	0.0508	-
37C	9	0.3	310	0.0074	0.0004	0.05044	-
		0.5	380	0.0001	0.0	0.08754	-
MATERIAL: TITANIUM, WET GRINDING							
I	9	0.3	260	0.540	0.0019	0.00359	-
II	9	0.3	180	0.290	0.0012	0.00401	-
III	9	0.3	240	0.824	0.0031	0.00373	-
37C	9	0.3	160	0.397	0.0015	0.00389	-

FIG. 6

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SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C09K3/14   C04B35/565   B24D3/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C09K   C04B   B24D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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E	EP,A,0 609 864 (LONZA A.G.) 10 August 1994 see claims 1-10 see column 2, line 2 - line 9 see column 3, line 5 - line 22 see example 1 ---	1,34, 36-38
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A		1-36, 82-88

X	EP,A,0 178 753 (KENNECOTT CORPORATION) 23 April 1986 see claims 1-17 see column 7, line 23 - column 8, line 31 ---	82-88
	-/--	

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 November 1994	2 4. 11. 94

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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US-A-1937060		NONE		